

VOC Measurements at Thompson Farm and Appledore Island during ICARTT 2K4

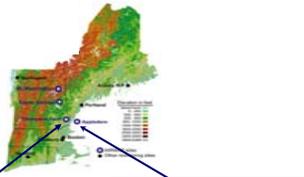
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A suite of hydrocarbons, halocarbons and alkyl nitrates were measured during the ICARTT 2004 campaign at two AIRMAP monitoring sites (Figure 1), Appledore Island (42.99 N, -69.34 W), 6 miles off the coast of NH and Thompson Farm (43.11 N, -70.95 W), 10 miles inland in Durham, NH. An automated GC system equipped with two electron capture detectors (ECDs) and two flame ionization detectors (FIDs) was used at Thompson Farm to sample ambient air pulled from the top of a 15 m tower every 40 minutes. Hourly canister samples were collected at Appledore Island from the top of a WWI1000 tower (20 m) July 1 through August 13, 2004. Canister samples were returned to the laboratory for analysis by gas chromatography using FID and ECD in conjunction with mass spectrometry. Two proton transfer reaction mass spectrometers (PTR-MS) were also deployed for VOC measurements at both sites.

Figure 1. Location of AIRMAP sampling sites.

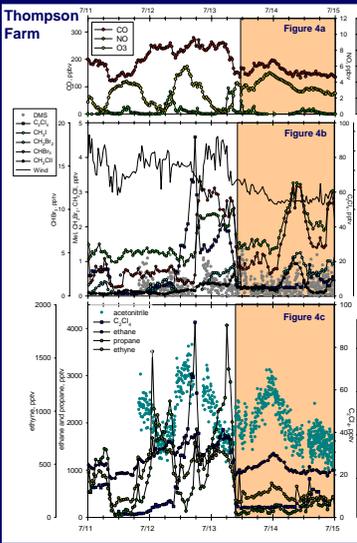


Sample collection and analysis

A GC system using two ECDs and two FIDs was used at Thompson Farm (Figure 2) for measurements of atmospheric NMHCs, halocarbons and alkyl nitrates every 40 minutes. The Thompson Farm GC system is designed for dual stage trapping using liquid nitrogen. The first stage cooling unit (-20 °C) contains an empty 6" x 1/8" silicoated sample loop while the second stage (-155 °C) contains a 6" x 1/8" silicoated sample loop filled with glass beads (60/80 mesh) for sample concentration. After the loops reach their initial set point temperatures, a 1000 cc sample is pulled from the sampling manifold. After a helium sweep used to remove ozone, the sample loop is isolated, rapidly heated to 100 °C, and then injected using a helium carrier gas. The sample stream is split into four, with each sub-stream feeding a separate GC separation column housed in a single gas chromatograph. For the standard analysis protocol, a 1000 cc (STP) aliquot from one of two working standards was assayed every ninth analysis.

Hourly canister samples were collected at Appledore Island (Figure 3) for C₂-C₁₀ NMHCs, C₂-C₁₀ halocarbons, C₂-C₁₀ alkyl nitrates and selected sulfur compounds. Canister samples were collected in 2-liter electroplated stainless steel canisters and pressurized to 30 psig using a single head metal bellows pump. Canister samples were returned to the laboratory for analysis by gas chromatography using two GCs (two FIDs and two ECDs) in conjunction with mass spectrometry. The samples are analyzed by cryotrapping 1200 cc (STP) of air on a glass bead filled loop immersed in liquid nitrogen. After the sample is trapped, the loop is isolated, warmed to 80 °C and the sample is injected. Helium carrier gas flushes the contents of the loop and the stream is split into five, with each sub-stream feeding a separate GC column. For the standard analysis protocol, a 1200 cc (STP) aliquot from one of two working standards is assayed every fifth analysis. The measurement precision for each of the halocarbons, hydrocarbons, alkyl nitrates and OVOCs is in the range of 0.1-12%.

The Thompson Farm PTR-MS measured a suite of VOCs by continuously subsampling a stream of the manifold air through a 6 ft x 1/8 inch I.D. PFA Teflon sampling line using a down stream sampling pump. The flow rate through the sub-sampling line is 2.5 L/min and the residence time of the air in the line is short (<1 s). The PTR-MS quantifies steps through a series of 30 masses in order to accurately identify and quantify the target gases. Of the 30 masses monitored at Thompson Farm, 6 masses are used for diagnostic purposes while the other 24 masses correspond to the VOCs of interest. On Appledore Island, air was drawn from 4m above the roof of the tower using a 100 ft x 3/8 inch O.D. PFA Teflon sampling line. The flow rate through the sample line was ~75 L/min, resulting in a residence time of ~2 s. A sub-stream of air flowing continuously fed the PTR-MS for the VOC measurements.



Forest Fires and Clean Marine Air

Measurements at Thompson Farm from July 11-15 reveal two distinct events. Air masses from the Alaskan wild fires were encountered at TF on the 12th of July as shown by sustained CO (Figure 4a) and elevated acetonitrile (Figure 4c). When the wind direction changed mid day on the 13th, a clean oceanic influence (Figure 4b, orange shaded region) was characterized by low C₂Cl₄, an anthropogenic tracer, and hydrocarbon mixing ratios (Figure 4c) along with elevated marine derived halocarbons (Figure 4b). The air mass encountered during this period had traveled from the North Atlantic (Figure 5a).

On the evening of July 12th C₂Cl₄ mixing ratios dropped to around 3 pptv at Appledore Island (Figure 6b, orange shaded region). They remained low until mid day on the 15th. During this period, the air masses sampled at Appledore Island had traveled from the mid-Atlantic then southwest along the coast of Maine (Figure 5b). Concentrations of CH₂Br₂, CH₂Br, CH₃ and CH₂ClI all increased during this period indicating coastal influence (Figure 6b).

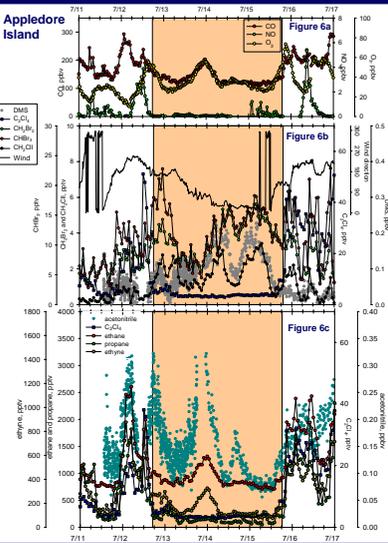
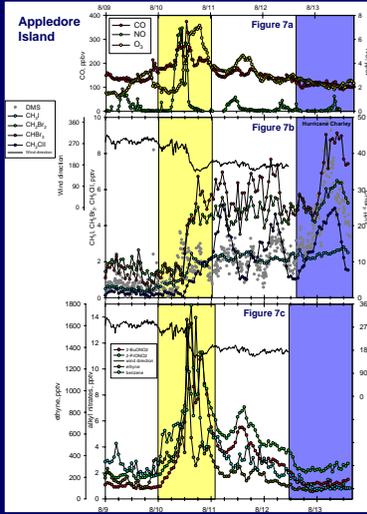


Figure 5. Back trajectory analysis for a) the evening of July 15th, 2004 for Thompson Farm and b) early on July 15th 2004 for Appledore Island.



Urban Influence and Hurricane Charley

On August 10th Appledore Island was influenced by a polluted air mass (yellow shaded region, Figures 7a,b,c). The air mass was characterized by high NO, CO and O₃ (Figure 7a) and elevated levels of alkyl nitrates and hydrocarbons (Figure 7c). Mixing ratios of halocarbons also increased mid day on the 10th as the wind direction shifted from the ocean (Figure 7b). Back trajectories indicate that the region was influenced by an air mass that traveled over the mid west and then up along the eastern seaboard (Figure 8a).

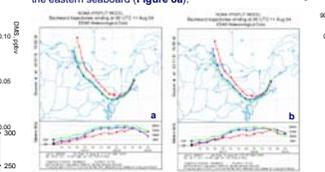


Figure 8. Back trajectory analysis for the evening of August 10th for a) Appledore Island and b) Thompson Farm.

On August 10th Thompson Farm was also influenced by the same polluted air mass (yellow shaded region Figure 9a,b,c). The air mass was further characterized by high CO and O₃ (Figure 9a) and elevated levels of hydrocarbons (Figure 9c). Mixing ratios of halocarbons and DMS increase mid day on the 11th as the wind direction shifted from the ocean (Figure 9b). Back trajectories indicate that the region was influenced by an air mass that traveled over the mid west and then up along the eastern seaboard (Figure 8b).

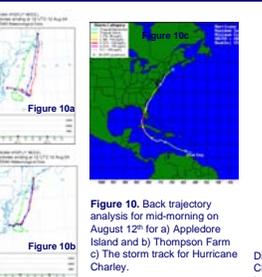
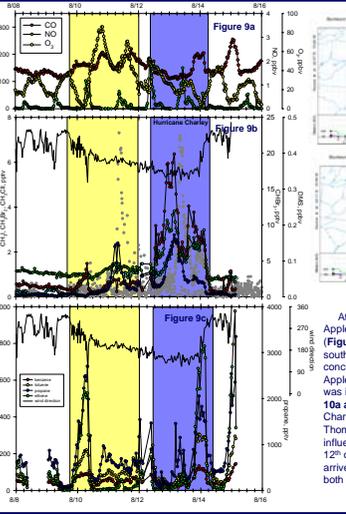


Figure 10. Back trajectory analysis for mid-morning on August 12th for a) Appledore Island and b) Thompson Farm. c) The storm track for Hurricane Charley.

At mid-day on August 10th, the winds at both Appledore Island (Figures 7b) and Thompson Farm (Figure 9c) shifted from out of the west to out of the south. This southerly flow brought increased concentrations of all halocarbons and DMS to Appledore. Back trajectories indicate that the air mass was in contact with the Mid-Atlantic US Coast (Figure 10a and b) that was at the time impacted by Hurricane Charley (Figure 10c). Both Appledore Island and Thompson Farm show evidence of Hurricane Charley's influence in the Northeast region beginning late on the 12th of August (blue shaded areas). Hurricane Charley arrived as a tropical depression with enhancements in both halocarbons and DMS.

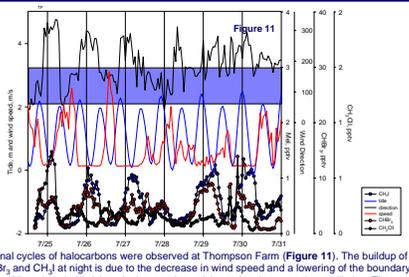


Figure 11. Diurnal cycles of halocarbons were observed at Thompson Farm (Figure 11). The buildup of CH₂Br and CH₃ at night is due to the decrease in wind speed and a lowering of the boundary layer. When the winds pick up in the morning, mixing ratios decrease due to dilution. The diurnal cycle of CH₂ClI sometimes coincides with this but is also affected by photolytic destruction during the daytime.

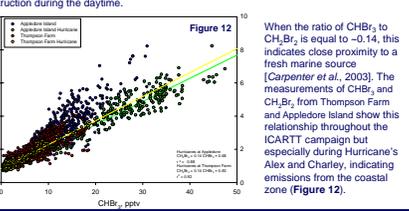


Figure 12. When the ratio of CH₂Br₂ to CH₂Br is equal to ~0.14, this indicates close proximity to a fresh marine source [Carpenter et al., 2003]. The measurements of CH₂Br and CH₂Br₂ from Thompson Farm and Appledore Island show this relationship throughout the ICARTT campaign but especially during Hurricane's Alex and Charley, indicating emissions from the coastal zone (Figure 12).

High Ozone at Thompson Farm

O₃ at Thompson Farm exceeded 110 ppbv on July 22nd (Figure 13a). Elevated mixing ratios of ethyne, C₂Cl₄, and alkyl nitrates were observed indicating a well-processed polluted air mass (Figure 13a and b). Back trajectory analysis indicates that the air mass traveled from the mid west to the east coast and up to Thompson Farm having come into contact with high population areas (Figure 14).

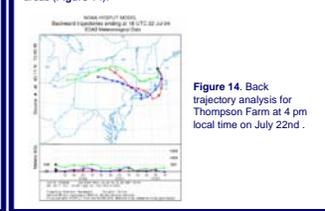


Figure 14. Back trajectory analysis for Thompson Farm at 4 pm local time on July 22nd.